

Nernst effect anisotropy as a sensitive probe of Fermi surface distortions from electron-nematic order

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We analyze the thermoelectric response in layered metals with spontaneously broken rotation symmetry. We identify the anisotropy of the quasiparticle Nernst signal as an extremely sensitive probe of Fermi surface distortions characteristic of the ordered state. This is due to a subtle interplay of different transport anisotropies which become additionally enhanced near van-Hove singularities. Applied to recent experiments, our results reinforce the proposal that the underdoped cuprate superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ displays such “electron-nematic” order in the pseudogap regime.

Spontaneous breaking of lattice rotation symmetry due to electronic correlations is currently in the focus of intense interest, most prominently in cuprate high-temperature superconductors such as $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ (Refs. 1–3) and in the metamagnetic metal $\text{Sr}_3\text{Ru}_2\text{O}_7$ (Ref. 4). In analogy to liquid crystals, a phase with broken rotation (but preserved translation) symmetry has been dubbed electron nematic.⁵

In cuprates, electron-nematic order has been discussed early on as intermediate phase which occurs upon melting of a uni-directional charge-density-wave (“stripe”) phase.^{5–7} Microscopically, it is one of the known instabilities of the two-dimensional (2d) Hubbard model.^{8–10} The first clear-cut signature of electron-nematic order in cuprates was found in neutron scattering experiments on $\text{YBa}_2\text{Cu}_3\text{O}_{6.45}$,¹ where the spin-fluctuation spectrum was found to develop a distinct anisotropic incommensurability below a temperature T of about 150 K. Earlier transport measurements on $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ (Ref. 11) also detected resistivity anisotropies ρ_a/ρ_b of order 2 in the underdoped regime, but remained less conclusive. The reason is that the crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ contains CuO chains which break the otherwise tetragonal symmetry of the CuO₂ planes. In an order-parameter language, this implies a small field which couples linearly to the nematic order parameter. This has two main effects: (i) potentially existing nematic order will be aligned and (ii) a nematic ordering transition will be smeared out. While (i) enables observables to show a macroscopic anisotropy, which might otherwise be masked by domain formation, (ii) implies that *electronic* nematic order and purely structural effects cannot be sharply distinguished. Remarkably, locally broken rotation symmetry has been found on the surface of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ and $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ using scanning tunneling microscopy.¹² In $\text{Sr}_3\text{Ru}_2\text{O}_7$, nematic order is a candidate explanation for the low- T phase which masks the metamagnetic critical endpoint at around 8 T.^{4,13} Resistivity anisotropies have been detected here, but a full picture has not yet emerged, because the rather unusual thermodynamics near the low- T phase boundaries is not understood.¹⁴

Very recent measurements^{2,3} of the Nernst effect,¹⁴ that is the transverse voltage induced by a thermal gradi-

ent in the presence of a magnetic field, have uncovered a surprisingly large anisotropy in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ below the pseudogap temperature. Consequently, this has been interpreted as evidence for broken rotation symmetry, but a theory which links this anisotropy to a particular ordered state was not available. Previously, the Nernst effect had been extensively studied as a probe of cuprate pseudogap physics,¹⁵ but mainly interpreted as sign of precursor superconducting fluctuations. Only recently, a second contribution to the Nernst signal has been identified and associated to quasiparticle physics.¹⁶ Theoretically, the quasiparticle Nernst effect in the presence of antiferromagnetic¹⁷ and stripe¹⁸ order has been investigated.

In this paper, we analyze, for the first time, the spatial anisotropy of the Nernst effect. We show that an enhanced and strongly anisotropic quasiparticle Nernst signal arises from the Fermi surface distortions which accompany broken rotation symmetry in metals. Surprisingly, small anisotropies in the kinetic energy can be easily enhanced by an order of magnitude in the Nernst signal, due the interplay of the anisotropies of conductivity and thermopower. A similarly large anisotropy does *not* arise from stripe phases. Hence, we establish the Nernst effect as a very sensitive and unique probe of electron-nematic order.¹⁹ Applied to the measurements on underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ (Refs. 2,3), we confirm the presence of the long-sought electron-nematic phase in the pseudogap regime.

Quasiparticle model. We shall calculate the thermoelectric response in a one-band model of quasiparticles. For concreteness, we work on a two-dimensional (2d) square lattice with a tight-binding dispersion

$$\begin{aligned} \varepsilon_{\mathbf{k}} = & -2t_1(\cos k_x + \cos k_y) - 4t_2 \cos k_x \cos k_y \\ & - 2t_3(\cos 2k_x + \cos 2k_y) - \mu. \end{aligned} \quad (1)$$

Such a 2d model is appropriate not only for cuprate superconductors, but (with some modifications) for a variety of other layered materials with tetragonal lattice structure, including $\text{Sr}_3\text{Ru}_2\text{O}_7$. To simplify calculations, we shall neglect inter-layer coupling, but will comment on its effect towards the end.

Nematic order distorts the band structure, which, on the mean-field level, can be captured by anisotropic hop-

ping parameters.^{8,10} Here we shall focus on the case of a $d_{x^2-y^2}$ electron nematic, as may arise from a Pomeranchuk instability in the $l = 2$ channel or as precursor of a stripe phase. We introduce an anisotropy parameter ϵ , such that the hopping matrix elements obey $t_{1x,y} = (1 \pm \epsilon/2)t_1$ and $t_{3x,y} = (1 \pm \epsilon/2)t_3$. For $\epsilon \neq 0$, the lattice symmetry is thus broken from C_4 down to C_2 .

Transport theory. The linear thermoelectric response is captured by three conductivity tensors $\hat{\sigma}$, $\hat{\alpha}$, and $\hat{\kappa}$, which relate charge current \vec{J} and heat current \vec{Q} to electric field, \vec{E} and thermal gradient, $\vec{\nabla}T$ vectors:

$$\begin{pmatrix} \vec{J} \\ \vec{Q} \end{pmatrix} = \begin{pmatrix} \hat{\sigma} & \hat{\alpha} \\ T\hat{\alpha} & \hat{\kappa} \end{pmatrix} \begin{pmatrix} \vec{E} \\ -\vec{\nabla}T \end{pmatrix}. \quad (2)$$

The electrical field induced by a thermal gradient in the absence of an electrical current can be expressed by the linear response relation $\vec{E} = -\hat{\theta}\vec{\nabla}T$, and Eq. (2) together with $\vec{J} = 0$ yields $\vec{E} = \hat{\sigma}^{-1}\hat{\alpha}\vec{\nabla}T$. Therefore, the Nernst signal ϑ_{yx} , defined as the transverse voltage E_y generated by a thermal gradient $\nabla_x T$, reads

$$\vartheta_{yx} = -\frac{\sigma_{xx}\alpha_{yx} - \sigma_{yy}\alpha_{xx}}{\sigma_{xx}\sigma_{yy} - \sigma_{xy}\sigma_{yx}} \quad (3)$$

and ϑ_{xy} is obtained from $x \leftrightarrow y$. For a magnetic field $\vec{B} = B\hat{z}$ in z direction, the Nernst coefficient is usually defined as $\nu_{yx} = \vartheta_{yx}/B$, which tends to become field-independent at small B . We employ a sign convention such that the vortex Nernst coefficient is always positive (formally $\nu_{xy} = -\vartheta_{xy}/B$, Ref. 20). In general, the Nernst coefficient can be negative or positive, for example if it is caused by the flow of charged quasiparticles.

The simplest description of quasiparticle transport is via the Boltzmann equation in the relaxation-time approximation. We assume a momentum and energy-independent relaxation time τ_0 , as is appropriate for elastic impurity scattering at low temperatures. Then, the electrical and thermoelectrical conductivities read:

$$\begin{aligned} \alpha_{xx} &= \frac{2e\tau_0}{T} \sum_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}^0}{\partial \varepsilon(\mathbf{k})} \varepsilon(\mathbf{k}) (v_{\mathbf{k}}^x)^2, \\ \alpha_{xy} &= \frac{2e^2 B \tau_0^2}{T \hbar c} \sum_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}^0}{\partial \varepsilon(\mathbf{k})} \varepsilon(\mathbf{k}) v_{\mathbf{k}}^x \left[v_{\mathbf{k}}^y \frac{\partial v_{\mathbf{k}}^y}{\partial k_x} - v_{\mathbf{k}}^x \frac{\partial v_{\mathbf{k}}^y}{\partial k_y} \right], \\ \sigma_{xx} &= -2e^2 \tau_0 \sum_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}^0}{\partial \varepsilon(\mathbf{k})} (v_{\mathbf{k}}^x)^2, \\ \sigma_{xy} &= -2 \frac{e^3 B \tau_0^2}{\hbar c} \sum_{\mathbf{k}} \frac{\partial f_{\mathbf{k}}^0}{\partial \varepsilon(\mathbf{k})} v_{\mathbf{k}}^x \left[v_{\mathbf{k}}^y \frac{\partial v_{\mathbf{k}}^y}{\partial k_x} - v_{\mathbf{k}}^x \frac{\partial v_{\mathbf{k}}^y}{\partial k_y} \right], \end{aligned} \quad (4)$$

where $e = |e|$ is the electron charge, $\mathbf{v}_{\mathbf{k}}$ the velocity, and $f_{\mathbf{k}}^0$ the Fermi function. In this approximation, the Nernst signal is linear in both T (at low T) and τ_0 . In the following, we shall be interested in the magnitude and anisotropy of the low- T Nernst coefficient, i.e., we shall use Eqs. (4) to calculate ν_{xy}/T and ν_{yx}/T .

Analytical considerations. On general grounds, the Hall conductivities obey $\sigma_{xy} = -\sigma_{yx}$ independent of

the crystal symmetry.²¹ Such a relation does not hold for $\alpha_{xy,yx}$ in general, however, in the low- T limit the Mott relation can be derived from Boltzmann theory,²² $\hat{\alpha} \propto d\hat{\sigma}/d\mu$, implying that $\alpha_{xy} = -\alpha_{yx}$. Any anisotropy in the Nernst signal is therefore arising from $\sigma_{xx} - \sigma_{yy} \neq 0$ and $\alpha_{xx} - \alpha_{yy} \neq 0$ – both will have a piece which is linear in ϵ . In general, the Nernst anisotropy at low T will depend on the anisotropies of the Fermi surface, of the Fermi velocities, and of the scattering rate (the latter anisotropy is not taken into account in our calculation).

It is worth noting one limiting result: For the simplest anisotropic dispersion, $\varepsilon_{\mathbf{k}} = (k_x^2/m_x + k_y^2/m_y)/2$ with $m_{y,x} = (1 \pm \epsilon/2)m$, the anisotropies of σ and α obtained in the Boltzmann framework (4) cancel in the Nernst signal, i.e., the Nernst signal remains zero due to Sondheimer cancellation.²³ ($\nu = 0$ is an artifact of an energy-independent τ_0 .) However, we shall obtain a large anisotropic Nernst response for non-parabolic dispersion.

Numerical results. We start with a survey of the Nernst signal in the C_4 -symmetric case. ν/T is shown in Fig. 1a as function of the chemical potential and the second-neighbor hopping t_2 , with t_3 kept zero. While ν/T is negative for all parameters, it is small for approximately circular-shaped Fermi surfaces, including the cases of small and large band filling for $|t_2/t_1| < 1/2$. (Note that ν/T remains non-zero in the limit of zero filling, as both the lattice effects and the Fermi energy vanish in this limit.) In contrast, the Nernst signal is large near the line $t_2 = \mu/4$ where the 2d van-Hove singularity is at the Fermi surface.

We now consider the sensitivity of the Nernst signal to a nematic distortion, i.e., a hopping anisotropy. Both ν_{xy}/T and ν_{yx}/T vary linearly with ϵ , thus we plot the relative linear variation $(1/\nu)d(\nu_{yx} - \nu_{xy})/d\epsilon|_{\epsilon=0}$ in Fig. 1b. As the Nernst signal itself, its variation is small near the band edges for $|t_2/t_1| < 1/2$, while it is large near the van-Hove singularity. Remarkably, in a large regime of parameters the relative variation is 2...5, i.e., the Nernst signal responds to anisotropies 2...5 times stronger compared to the kinetic energy. The sign of the anisotropy, $\nu_{yx} - \nu_{xy}$, is robust and such that the (negative) Nernst signal is enhanced if the thermal gradient is applied along the direction of stronger hopping.

Hole-doped cuprates are located at $-t_2/t_1 \approx 0.2 \dots 0.4$ and $\mu/t_1 = -0.5 \dots 0$, i.e., rather close to the van-Hove regime. We now discuss in more detail the thermoelectric response for such parameters. We choose $t_1 = 0.38$ eV and present results as function of hopping anisotropy for different (fixed) band fillings n and different $t_{2,3}$. In $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$, the bare hopping anisotropy extracted from band-structure calculations is $|\epsilon| \approx 3 \dots 4\%$ with $t_a < t_b$ (i.e. $\epsilon < 0$ for \hat{x} along the crystalline a axis) – this effect is primarily due to the coupling between planes and chains.²⁴ Nematic order is expected to strongly amplify this anisotropy, and theoretical treatments have suggested anisotropies up to $|\epsilon| = 20\%$.¹⁰

Fig. 2 shows the anisotropic elements of the response tensors $\hat{\sigma}$ and $\hat{\alpha}$, together with the Nernst coefficient, for

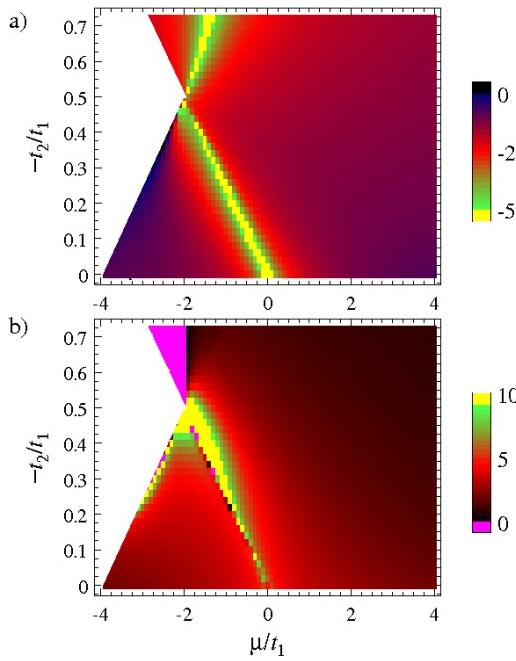


FIG. 1: Evolution of the Nernst effect as function of chemical potential μ and second-neighbor hopping ($-t_2/t_1$). a) Nernst signal ν/T in the isotropic case, in units of $2.45 \times 10^3 \text{V}/(\text{K}^2\text{T}) \times \tau_0/\text{s}$ for $t_1 = 1 \text{eV}$. b) Relative linear change of the Nernst signal with hopping anisotropy, $d(\nu_{yx} - \nu_{xy})/(\nu d\epsilon)$. In both panels, the white area corresponds to an empty band. For $-t_2/t_1 > 1/2$ the band minimum moves to $(0, \pi), (\pi, 0)$. For $t_2 = \mu/4$ the van-Hove singularity is located at the Fermi level, where both the Nernst signal and its sensitivity to anisotropy are maximum. (Very close to this line the data are inaccurate due to discretization errors.) By particle-hole symmetry, the data for $t_2/t_1 > 0$ can be read off using $\mu \rightarrow -\mu$.

$t_2/t_1 = -0.4$, $t_3 = 0$ and band filling $n = 0.86$. While the anisotropy in the longitudinal conductivity $\sigma_{xx,yy}$ is moderate, Fig. 2a, there is a substantial anisotropy in $\alpha_{xx,yy}$, Fig. 2b. Remarkably, both anisotropies constructively interfere to generate a large Nernst anisotropy, Fig. 2c. The signal peaks at some finite ϵ where the Fermi-surface topology changes as a function of the anisotropy – this point again corresponds to a (now anisotropic) van-Hove singularity. Note that ν_{xy} can even change sign at some finite ϵ , leading to a formal divergence of ν_{yx}/ν_{xy} . (Other additive contributions to ν , e.g., from pairing fluctuations, may render this statement insignificant.)

A few remarks are in order. First, the thermopower $S = \alpha_{xx}/\sigma_{xx}$ comes out to be negative, Fig. 2b, also for $\epsilon = 0$. This is in contrast to the common wisdom that a single hole-like Fermi surface leads to a positive thermopower. Indeed, we obtain a positive (negative) thermopower in the limits of large (small) band filling, but the sign change in the $\mu-t_2$ plane is *not* tied to the topological change of the Fermi surface (i.e. the van-Hove singularity), but instead occurs above half filling for $t_2 < 0$. Second, the sign of the anisotropy in σ , Fig. 2a, is robust. This is physically transparent: $t_x > t_y$ implies a larger

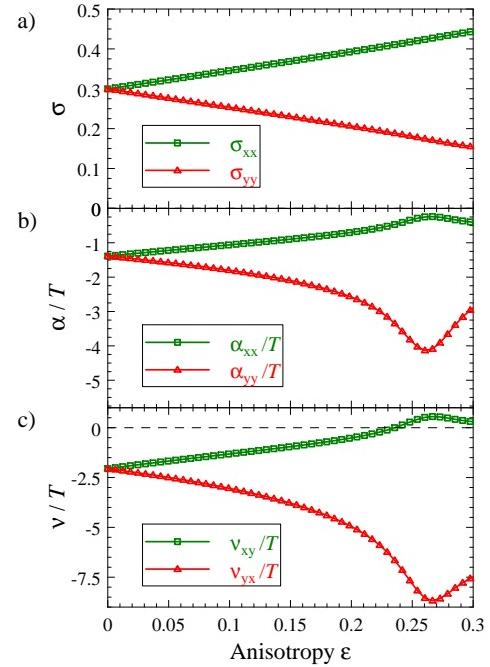


FIG. 2: Anisotropic response functions for nematic order, with hopping anisotropy ϵ . The hopping parameters are $t_1 = 0.38 \text{eV}$, $t_2 = -0.4t_1$, $t_3 = 0$, the band filling is fixed to $n = 0.86$. a) Longitudinal conductivity σ_{xx} , σ_{yy} and b) thermoelectric tensor α_{xx}/T , α_{yy}/T ; c) Nernst coefficient ν_{xy}/T , ν_{yx}/T . The units are σ [$3.19 \times 10^{20}/(\Omega\text{m}) \times \tau_0/\text{s}$] (using the c-axis lattice constant of $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$), α/T [$2.36 \times 10^{12}\text{V}/(\text{K}^2\Omega\text{m}) \times \tau_0/\text{s}$], ν/T as in Fig. 1.

velocity along \hat{x} , and hence generically $\sigma_{xx} > \sigma_{yy}$. Third, the sign of the anisotropy ($\alpha_{xx} - \alpha_{yy}$), Fig. 2b, changes in the $\mu-t_2$ plane exactly at the van-Hove singularity. Notably, in Eq. (3) this sign change is compensated by the similar sign change of the Hall conductivity σ_{xy} , such that sign of the Nernst anisotropy is robust.

The influence of model parameters is illustrated in Fig. 3. For finite $t_3/t_2 < 0$, the van-Hove singularity is outside the regime of ϵ and n which is relevant for cuprates. (This conclusion may be changed by bilayer splitting, see below and Ref. 10.) Fig. 3 also makes clear that the response of ν/T to moderate anisotropies is strongly non-linear near a van-Hove point.

Discussion. The large Nernst anisotropy for a nematic state prompts the question how this compares to other states with rotation symmetry breaking. For cuprates, the prime candidate is stripe order. Following Ref. 18, we have also calculated the Nernst anisotropy in various stripe states with real-space period 8 and 16. In most cases, the Nernst anisotropy for realistic parameter values is moderate, i.e., less than a factor of two. Exceptions are states with extremely elongated Fermi pockets, which we only encountered for period-4 charge-only stripes (and for which no evidence exists in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$). Hence, stripe order is unlikely to explain the large Nernst anisotropy in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$.³

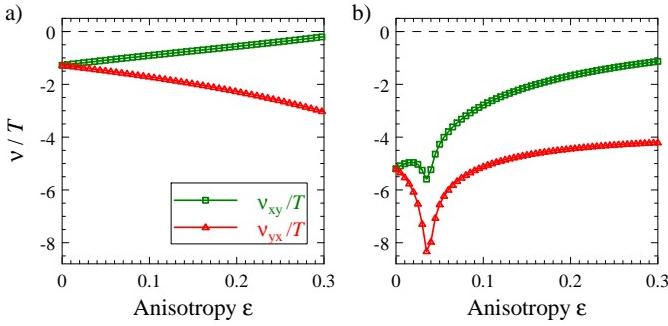


FIG. 3: Nernst coefficient ν/T as function of the hopping anisotropy ϵ , for parameters $t_1 = 0.38$ eV and a) $t_2 = -0.32t_1$, $t_3 = -0.5t_2$, $n = 0.875$, and b) $t_2 = -0.2t_1$, $t_3 = 0$, $n = 0.875$. The units are as in Fig. 1.

We thus confirm the interpretation of the data in Ref. 3, attributing the large anisotropy for $80\text{ K} < T < 150\text{ K}$ to a nematic state (while stripe-like order may set in at lower temperatures). Indeed, using $\epsilon = -0.2$ from Ref. 10, we can semi-quantitatively match the experimental results for $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$: We obtain a resistivity anisotropy $\sigma_b/\sigma_a \equiv \sigma_{yy}/\sigma_{xx} \approx 1.5 \dots 2.5$ (Ref. 11) and a Nernst anisotropy $\nu_b/\nu_a \equiv \nu_{xy}/\nu_{yx} \approx 4 \dots 10$ (Ref. 3).

Let us briefly discuss effects which were neglected in our calculation. A vertical dispersion from inter-layer coupling will smear the 2d van-Hove singularity, i.e., will remove the sharp peak in the Nernst signal as function of filling or distortion. However, as the Nernst signal is enhanced and very sensitive to anisotropy over a large

range of parameters, this will not qualitatively change our conclusions. For $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$, the main effect of inter-layer coupling is a bilayer splitting of the dispersion, which will move one of the van-Hove singularities closer to the physical parameter regime, likely enhancing the Nernst signal. Finally, at elevated temperatures, the scattering rate will be both anisotropic and energy-dependent. While it is known for cuprates that the antinodal scattering rates become much larger than the nodal ones, our conclusions would only be modified if the scattering near the two inequivalent *antinodes* becomes different by a factor of order 5 – this we consider unlikely.

Conclusions. Our key result is a surprisingly large sensitivity of the Nernst anisotropy to symmetry-breaking Fermi-surface distortions, rendering the Nernst effect a unique tool to detect electron-nematic order. The effect is particularly strong for non-parabolic band dispersion, as occurs near van-Hove singularities and/or half-filling. We have provided a concrete theory for the measured Nernst anisotropies in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$,^{2,3} pointing towards electron-nematic order in the pseudogap regime. We propose to search for Nernst anisotropies in other candidate compounds for such order, such as $\text{Sr}_3\text{Ru}_2\text{O}_7$. Our results in Fig. 2 suggest that anisotropies of the thermopower are worth investigating as well.

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- ¹ V. Hinkov *et al.*, Science **319**, 597 (2008).
² L. Taillefer, Keynote lecture, M2S-IX Conference, Tokyo (Sep 9, 2009).
³ R. Daou *et al.*, preprint arXiv:0909.4430.
⁴ R. A. Borzi *et al.*, Science **315**, 214 (2007).
⁵ S. A. Kivelson, E. Fradkin, and V. J. Emery, Nature **393**, 550 (1998).
⁶ S. A. Kivelson *et al.*, Rev. Mod. Phys. **75**, 1201 (2003).
⁷ M. Vojta, Adv. Phys. **58**, 699 (2009).
⁸ H. Yamase and H. Kohno, J. Phys. Soc. Jpn. **69**, 332 and 2151 (2000).
⁹ C. J. Halboth and W. Metzner, Phys. Rev. Lett. **85**, 5162 (2000).
¹⁰ H. Yamase and W. Metzner, Phys. Rev. B **73**, 214517 (2006).
¹¹ Y. Ando *et al.*, Phys. Rev. Lett. **88**, 137005 (2002).
¹² Y. Kohsaka *et al.*, Science **315**, 1380 (2007).
¹³ S. A. Grigera *et al.*, Science **306**, 1154 (2004).
¹⁴ K. Behnia, J. Phys.: Condens. Matter **21**, 113101 (2009).
¹⁵ Y. Wang, L. Li, and N. P. Ong, Phys. Rev. B **73**, 024510 (2006).
¹⁶ O. Cyr-Choinière *et al.*, Nature **458**, 743 (2009).
¹⁷ A. Hackl and S. Sachdev, Phys. Rev. B **79**, 235124 (2009).
¹⁸ A. Hackl, M. Vojta, and S. Sachdev, preprint arXiv:0908.1088.
¹⁹ A probe which directly couples to the bulk quadrupolar order parameter of an electron-nematic phase is usually not available.
²⁰ For fixed magnetic field $\vec{B} \parallel \hat{z}$, a C_4 -symmetric situation yields $\vartheta_{xy} = -\vartheta_{yx}$ from Eqs. (2,3). Here we adopt the convention (also used experimentally) that the three vectors \vec{E} , $\vec{\nabla}T$, and \vec{B} form a right-handed system for the measurements of both ν_{xy} and ν_{yx} , which may be achieved by switching the sign of the magnetic field. Then, $\nu_{xy} = \nu_{yx}$ for C_4 symmetry.
²¹ This follows from the Kubo expressions for $\sigma_{xy,yx}$ or, for low T , from the geometric interpretation of the Hall conductivity, see: N. P. Ong, Phys. Rev. B **43**, 193 (1991).
²² N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Harcourt Publishers, Orlando, 1976.
²³ E. H. Sondheimer, Proc. R. Soc. London, Ser. A **193**, 484 (1948).
²⁴ O. K. Andersen and T. Saha-Dasgupta, unpublished.